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Encapsulating Quantum Dots into ZnO Nanorods for Advanced photonics and Laser Applications

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14. ABSTRACT
What significant findings came from this project:
We demonstrated the encapsulation of luminescent quantum dots (QDs) in ZnO nanorods grown by acqueous solution. The QDs adsorbed on the nanorod surface show enhanced photoluminescence. The QDs encapsulated into the ZnO nanorods show a wavelength shift and a decrease in photoluminescence. The project demonstrated the possibility to embed QDs emitting in various frequency ranges into ZnO Nanorods to produce solid state colorful light sources.
What is/are the significance of the findings:
The findings are a first step demonstrating the benefit of encapsulation of QDs in ZnO nanorods for advanced photonic applications. The wavelength shift observed in the photoluminescence indicates the effect of the ZnO nanorods on the emission on the quantum dots.
What new research questions came about from this project:
The strong enhancing effect due to the whispering gallery mode was not found. The questions are:
1) Is the whispering gallery mode depressed due to the poor quality of the ZnO surfaces grown in acqueous solution?
2) Are the QDs affecting the local properties of the ZnO crystals?

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Abstract Colloidal quantum dots are promising for new-generation light-emitting devices and lasers. By encapsulating quantum dots with various emission colours into single-crystal ZnO nano/microrods grown in chemical bath we obtain Fabry-Perot type resonances of the light emitted when stimulated by an external laser. The hexagonal structure of ZnO crystals act as optical cavity, and due to the waveguide effect partial photons would propagate along the nano/microrods axis direction. In order to grow patterned and ordered ZnO nano/microrods for Fabry-Perot type resonance, we developed a microsphere lithography technique to produce shadow masks onto GaN substrates. In this way we have been able to grow vertical ZnO nano/microrods arrays with controllable interspace and size by a simple aqueous solution method. We demonstrate the encapsulation of quantum dots (QD) into the ZnO nano/microrods by a regrowth process. The optical properties of the single rod, and of the ensemble of the structures are measured by photoluminescence, showing a clear enhancement of the light emitted by QD adsorbed on the rod surface, and a wavelength shift coupled to an intensity reduction after the encapsulation. This study is the first step towards the development of color-tunable lighting devices and lasers based on micro/nanorods, and will open the way to a plethora of applications in optoelectronics, medicine, and gas sensing.

Introduction

ZnO gained a great deal interest in the research community in last decades, as can be seen from the surge in the number of relevant publications. ZnO has many outstanding characteristics, such as a large direct band gap (3.37 eV), high excition binding energy (60 mV), high mechanical strength, transparency to visible light, piezoelectricity especially for high frequency and thermal stabilities at room temperature. ZnO crystallizes in the wurtzite structure with hexagonal unit cell (space group C6mc and lattice parameters a = 0.3296, and c = 0.52065 nm)[1]. One-dimensional semiconductor nanorods, as a key member of wurtzite zinc oxide formation representing a new class of materials, attracted great attation due to their quantun confinement properties[2]. Nanorods have promising potentials in a wide range of applications and are the fundamental building blocks for fabricating sensors[3,4,5], short–wavelength nanolasers[6], solar cells[7], light emitting diodes (LEDs)[8,9 ,10,11] , etc. Since 2001, when the first nanowire laser was reported in Science[12], more and more reserachers are

attracted towards this field[13,14]. Manipulation of photons in semiconductor bulk crystals and thin films has culminated in breakthroughs leading to the development of LEDs and solid-state lasers. Nanorods offer the double possibility to generate and to confine photons at the same time, by exploiting the spontaneous emission of the cavity material. Unfortunately, due to the limited number of semiconductors available for nanorod emitters, the current technology provides limited choices of wavelength range, emission efficiency, and reliability for practical applications. Revolutionary new approaches are needed to broaden the choices for system designers, and to significantly improve the existing technology.

Quantum dots (QDs) are semiconductor nanocrystals with size-dependent optical properties[15]. Their typical diameter is in the range 2-10 nm, giving features originated from the quantum confinement of electrons. The bandgap of QDs is possible to tune the light emission by controlling the size of the nanocrystal[16,17,18]. Light emission frequencies increase with the decrease of the quantum dot size, providing a way to tune the optical properties.

In this article we discuss how to encapsulate colloidal QDs as light sources into single-crystal ZnO nano/microrods (NMRs), which is the premise and base to develop novel devices such as LEDs and micro/nano lasers. Conventional LEDs have a number of drawbacks such as: (1) unsatisfactory thermal stability as the emission intensity reduces with temperature increasing; (2) limited choices for emission wavelength; (3) difficulty in miniaturizing the size for on-chip integration. To overcome this problem, QDs as emitters are encapsulated into single-crystal ZnO NMRs acting as optical resonators. The NMR laser with QDs as emitters has a number of options to select the desired wavelength. For example, multi-color emissions from a single NMR can be achieved by loading different types of QDs into the same NMR cavity. Light in the NMR can be reflected by the two ending facets to give rise to Fabry-Perot (FP) type resonances as shown in Fig. 1a. The FP-type lasing effect from a NMR is pictorially represented in Fig. 1b. Light confined by the side facets of a hexagonal NMR can instead give rise to whispering-gallery mode (WGM) resonances[19], as illustrated in Fig. 1c. Lasing in FP type requires a higher excitation threshold compared to the WGM, for the light stimulated along the Z axis of a hexagonal ZnO NMR is confined by total-internal reflections according to previous theoretical and experimental studies[20,21]. The use of QDs as laser gain media can avoid some of the negative aspects associated with traditional semiconductor lasers based on bulk or quantum well active media. For example, QDs have stronger exciton-photon coupling strength and higher thermal stability of luminescence compared to the bulk semiconductor crystal. In this research a low temperature aqueous-solution method will be used to grow ZnO NMRs. The low-temperature growth technique avoid thermal damage to the QDs and produce nanostructures with excellent physical properties. The features of ZnO NMR, like 1D geometry, dislocation-free single-crystalline nature, high refraction index and atomically smooth surface, allow for sufficient end-facet reflectivity and photon confinement. The strong field localization inside wavelength volumes is expected to boost the electron-light interaction within the emitter material. To the best of our knowledge, encapsulation of QDs into single-crystal NMRs has not been reported by others.

The all-solution process used for the preparation of ZnO NMRs and QDs can be easily scaled up with substantial savings in term of cost, energy and pollution compared to the standard

metal organic chemical vapor deposition. We believe that the concept of integrating QDs into ZnO NMRs for lighting and lasing applications will not only open a new research direction in fields of photonics and optoelectronics but also result in novel lighting devices that have both civil and military applications.

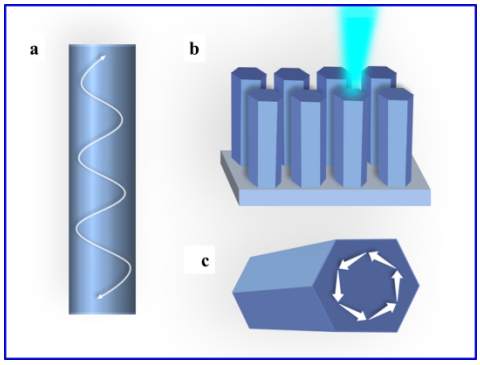

Figure. 1. (a) and (b) Illustrations for the FP type optical resonances within a NMR and lasing from a NMR, respectively. (c) Illustration for WGM resonances within a hexagonally-shaped NMR.

Experiment:

a) Growth of Vertical ZnO NMRs on GaN Substrate by Microsphere Lithography

Materials: $Zn(NO_3)_2 \cdot 6H_2O$ (99.5% purity, Aldrich), hexamethylenetetraammine (HMTA) (99.5% purity, Aldrich), Poly(methyl methacrylate) (PMMA) microsphere, with a diameter of 3.36 μm was purchased from Alfa Aesar and used as received.

We grow vertical ZnO NMRs onto patterned GaN substrates, with a method similar to the one reported by Dong et al[22]. Firstly, a monolayer of PMMA microspheres was self-assembled on a wafer surface by dip-coating, and then transferred to the GaN substrate (Fig 2a). After being dried in air, the PMMA microspheres formed a hexagonal pattern. After slightly melting the microspheres by thermal treatment at 140 °C to increase the masked area (Fig 2b), a layer of diluted TiO_x sol-gel was spin coated onto the PMMA/GaN substrate (Fig 2c) to fill the gaps between PMMA microspheres with a speed of 4000 rpm for 80 s. The TiO_x sol-gel was first synthesized from the precursors of titanium(IV) isopropoxide, 2-methoxyethanol and ethanolamine[23]. After waiting for more than 3 h for the solidification of the TiO_2 sol-gel, the microspheres were completely removed by sonication in DMF solvent for 30 min (Fig 2d). A regular pattern of holes was obtained. We adjusted the diameter of the holes by controlling the parameters of the thermal treatment in the drying cabinet of the GaN substrate with the PMMA microsphere layer. By varying the treatment temperature and the concentration of TiO_x sol-gel, the inner diameter of the hole template can be tuned conveniently. To grow patterned ZnO NMRs arrays, the GaN substrate with the hole template was fixed up-side down floating on top of the aqueous solution of 30 mM $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA. Then, the reaction vessel was sealed and kept at a 75 °C for 6 h. Finally, the sample was taken out, rinsed in deionized water and dried in air (Fig 2e).

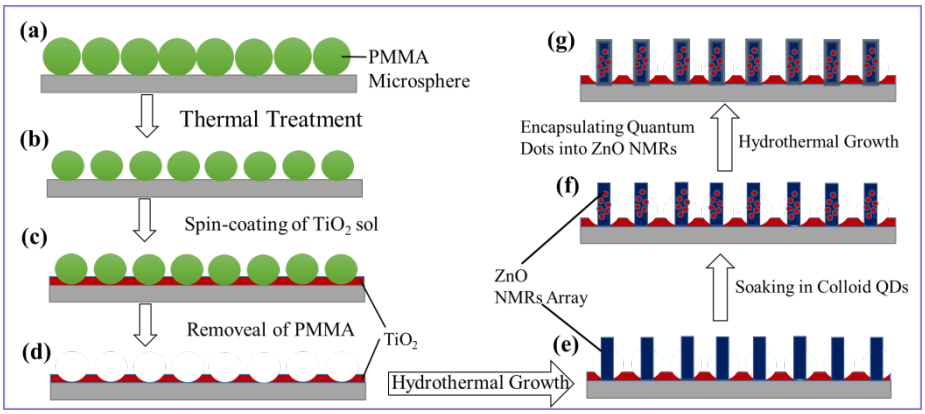

Figure 2 Schematic illustration of the fabrication process of patterned ZnO NMRs arrays.

b) Encapsulating QDs into ZnO NMRs

Firstly, QDs were attached to the surface of NMRs (Fig 2f). The ZnO/GaN substrates were dipped in a solution of CdSe colloidal QDs in n-hexane (QDs:n-hexane=1:20) at room temperature for 15 min, then the samples were rinsed with ethanol and dried at 50 °C. The attachment of QDs onto the NMRs surfaces occur by electrostatic interaction. Secondly, a new growth of ZnO was performed in a more diluted solution, containing 15 mM $Zn(NO_3)_2 \cdot 6H_2O$ and HMTA at 75 °C for 3 h.

Surface morphologies and microstructures of the samples were characterized by Field-emission scanning electron microscopy (FE-SEM, Zeiss Sigma), Helium Ion Microscope (HIM, Zeiss Orion NanoFab), Transmission Electron Microscopy (TEM, JEOL-2010) and Energy Dispersive X-ray spectrometer (EDS). Micro-Photo Luminescence (Micro-PL) measurements were performed to study the optical resonances at room temperature with a Renishaw inVia spectrometer using a 532 nm laser.

Results and Discussion

Growth of ZnO NMR Arrays and Encapsulation of QDs

The experimental results of vertically-grown ZnO NMRs on the GaN substrate are shown in Fig. 3. The results show that ZnO NMRs arrays are not highly ordered, because of the size inhomogeneity and the non-perfect packing of the PMMA microspheres, which can be appreciated from the SEM image of the spheres (Fig3a) and of the holes produced in the protecting layer after their removal (Fig 3b). Close-view and cross-sectional view SEM images (Fig 3c, 3d and 3e) reveal the hexagonal cross section of ZnO NMRs and the faceted prismatic morphology at the tip. This crystallite shape is due to the difference in the growth rate of the various crystal facets[24,25,26]. It is well known that the ZnO growth rate is faster in the <001> direction, and slower in the <101> direction. Growth along the <100> has the smallest rate. That will normally result in the formation of ZnO NMRs with hexagonal structure and constant cross section. However, it should be considered that, during the formation of ZnO crystals, the reactant concentration is progressively reduced, causing a shrinkage in the ZnO NMR cross section. This morphology however, does not affect the encapsulation of QDs, as confirmed by the HIM images (Fig 4) and the photoluminescence

obtained in ZnO NMRs[21,12]. Good optical performance lies on efficiency of the gain medium, surface quality and reflectivity properties of the optical cavity[20]. The relative optical properties of NMRs will be discussed later. QDs were then attached to the surfaces of NMRs by soaking. As shown in Fig 3f, both the substrate and ZnO NMRs are coveresd with QDs Better images obtained by HIM are shown in Fig 4a and 4b, whichclearly show that QDs at times agglomerate [27] but attach well on the ZnO NMRs surfaces. QDs were encapsutated into ZnO NMRs after regowth. The HIM images after this step are shown in Fig 4c and 4d. We can find that the surfaces of ZnO nanorods are rough after the ZnO regrowth and some areas are not covered by ZnO. By modifying the concentration of the solution for regrowth and the growth duration, complete encapsulation of QDs into the NMRs can be achieved.

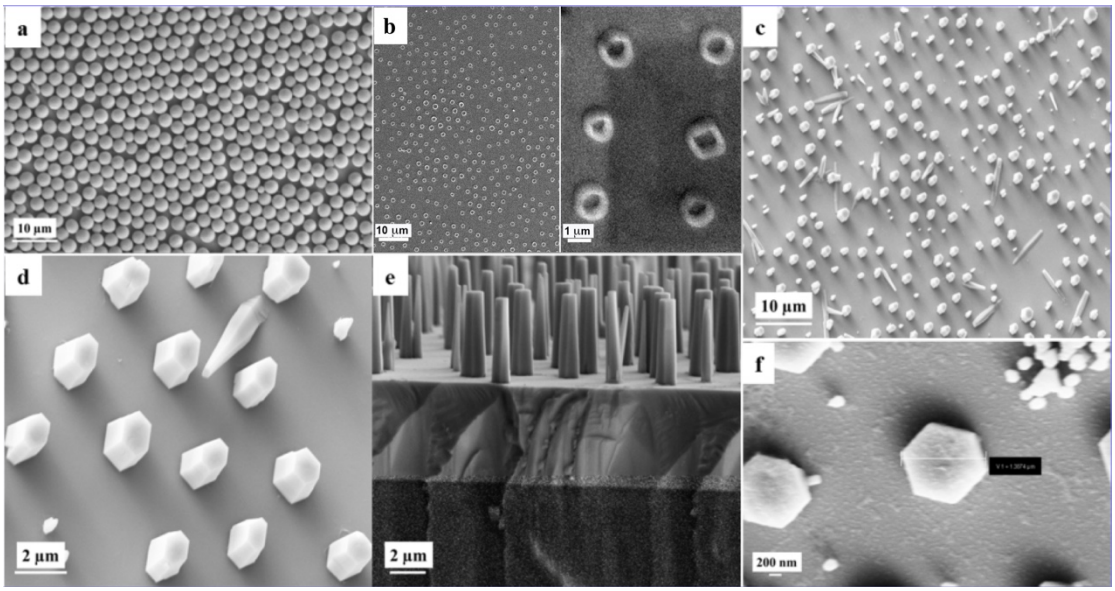

Figure 3. FE-SEM images show the process of growing vertical ZnO NMRs on GaN substrate and attaching QDs on ZnO NMRs surfaces. (a) highly ordered monolayer of PMMA microspheres self-assembled on the GaN substrate, (b) Microporous TiO_2 ring template obtained after removing PMMA microspheres. (c) Large scale, (d) Close-view and (e) Cross-section of ZnO NMRs grow on GaN substrate. (f) A close-view of the NMRs with QDs attached to their surfaces.

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Figure 4. HIM images show encapsulation QDs into ZnO NMRs. (a) Top-view and (b) QDs attached on the rod surfaces. (c) side-view and (d) top-view of a single ZnO rod after QDs encapsulation.

In order to check the quality and adhesion of CdSe QDs on the ZnO NMRs surfaces, we used TEM and EDX. High-resolution TEM allows us to qualitatively probe the internal structure of the ZnO NMRs and composite QDs and to determine QDs distribution in ZnO NMRs surface. Figure 5 shows that QDs are randomly distributed on the top and side of ZnO NMRs. The QDs and ZnO in the micrographs show well resolved lattice fringes. The hexagonal ZnO structure has lattice parameters a = 0.3296 and c = 0.52065 nm, so the lattice spacing of 0.261 nm found in the solid matrix (Fig 5c) corresponds to the (002) plane of ZnO in the wurtzite phase. This centro-symmetric structure of ZnO results in some special properties, amongst others, the piezoelectricity and pyroelectricity[28,2,29]. In the CdSe QDs we found lattice fringes spacings of 0.255 and 0.328 nm (Figure 5d), which matches perfectly with the interplanar distances of the (102) and (101) planes of CdSe[7]. O, Zn, Se, and Cd elements are present in the EDX spectrum (Figure 5d) and Table 1, confirming the existence of CdSe QDs in the ZnO microrods. The intensities of Cd and Se elements are quite weak compared to the O and Zn elements, due to the small quantity and random distribution of CdSe on ZnO microrod surfaces, as clearly shown by the TEM image in Figure 5a. The above discussion confirms the successful attachment of CdSe QDs on ZnO NMRs.

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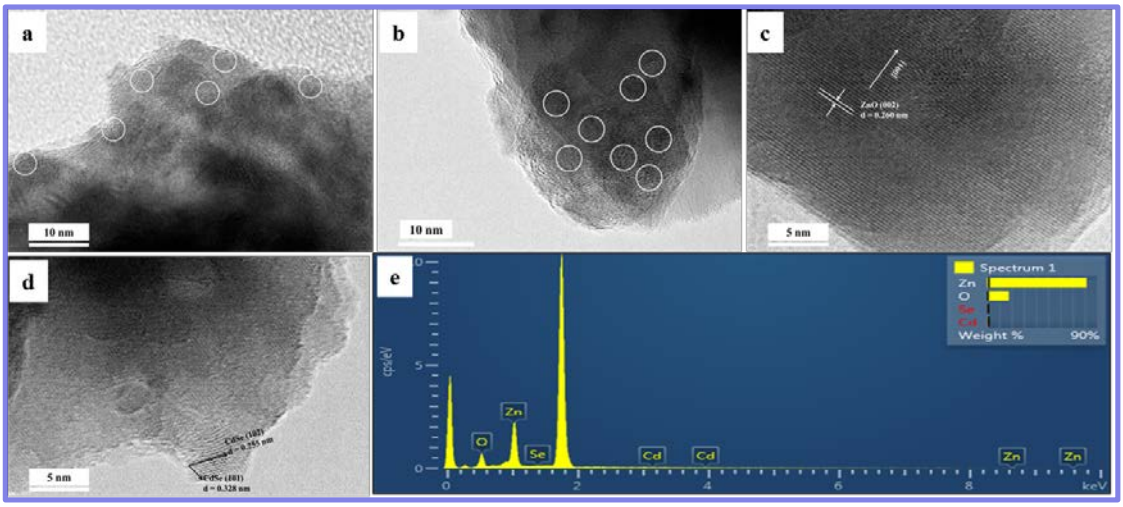

Figure 5. (a, b) TEM, (c, d) HR-TEM and (e)EDX result of the QDs on ZnO NMRs surfaces.

Table 1.EDX results of QDs on ZnO NMRs surfaces

Atomic species	O	Zn	Se	Cd	
Relative content (%)	17.89	81.42	0.36	0.34	100.00

Micro-photoluminesence of a single ZnO NMR containing QDs

The photoluminescence (PL) measurements were performed at room temperature using a Xe lamp with an excitation wavelength of 532 nm. The results are shown in Fig 6. Micro-PL was measured on single vertical ZnO NMRs grown onto GaN substrate. Three kind of samples were studied: ZnO NMR with small size QDs (Noted as QDs1 or QDs2) attached to surface (QDs1/s2 on ZnO NMR), ZnO NMR with embedded QDs1 (QDs1/s2 in ZnO NMR), colloidal QDs1 dispersed on a GaN substrate (QDs1/s2). The insets in Fig 6 are optical microscope images. The diameter of the rods is estimated to be 1.3 μm from SEM images. A laser beam with a spot size of about 1 μm was aimed perpendicularly to one of the NMRs and the QDs inside or attached to the NMR surface were excited to produce luminescence. ZnO NMR is transparent to visible light, and emissions from QDs can undergo multiple reflections in a ZnO NMR. ZnO is a birefringent crystal with a refractive index of about 2.45 in the visible range. Due to the waveguide effect a good fraction of the photons would propagate along the NMR Z-axis direction. Hence, inside the NMR, light rays refracted to the top upper facet give contribution to the micro-PL signal (Fig 1a). Light rays with different polarizations have different transmittance when refracted from ZnO to air. The micro-PL spectrum of colloidal small size quantum dots (QDs1) shows a single emission band centered at 580 nm (black curve in Figure 6a). There are two weak peaks at 547 nm and 561 nm, respectively, which have been attributed to the defect emission of ZnO NMR[13,30,31,32]. The intensity of

defect emission depends on the ZnO nanorod diameter[33,34]. A similar situation is found in Fig 6b 6c. It is evident that large quantum dots (QDs1) give origin to a band centered at 580 nm, while small quantum dots (QDs2) give origin to a band centered at 630 nm. The position of these peaks change a bit when the QDs are attached to the surface, while a noticeable blue-shift (20 nm) towards larger wavelength is observed for both kind QDs when they are embedded in the NMR (green curves). This effect could be attributed to the fact that the ZnO NMR acts as an optical cavity, creating a waveguide and FP type resonances, thereby shifting the wavelength towards higher values. It must also be noticed that after encapsulation the peaks are weaker, probably due to defects present at the NMR surface.

Normally, the larger the cavity size, the higher the resonance quality[21,35,36] . Figure 6b shows the related micro-PL spectrum of large size quantum dots (QDs2). The inset in Fig 6b is an optical microscopy image, in which the relatively thick rod marked by the cross was the target for collecting micro-PL spectra. The emission peak at 666 nm is pronounced, and its position is substantially unchanged after the attachement to the surface of the NMRs. After encapsulation, the peak intensity reduced and its position is red-shifted to 674 nm. By mixing the two sizes of QDs we find both peaks with the same characteristics, however we notice a strong intensity increase of the 580 nm peak, which is probably due to to a resonance in the ZnO rod. It means any types of QDs can be successfully encapsulated into ZnO NMRs. Lasers and LEDs of desired colour are likely to be achieved after encapsulating QDs with appropriate dimension.

Figure 6: Photoluminescence spectra in the visible range of ZnO NMRs before and after attachment of CdSe QD of different sizes (a) QDs1, (b) QDs2, (c) mixed QDs1 and QDs2.

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Conclusions

Encapsulation of QDs into a single crystal ZnO NMR provides a new route towards the novel optical devices. QDs of two different sizes are used as an example to study this process in ZnO NMRs grown in aqueous solution at low temperature. Our two-step aqueous epitaxial growth process results in complete encapsulation of QDs. Our study indicates that in principle any kind QDs can be incorporated into ZnO MNRs. The epitaxial growth over ZnO NMR surface leads to the encapsulation of QDs into the crystal while maintaining the single crystal feature. We believe that QDs can be encapsulated not only into ZnO, but also into any other functional crystals grown by the epitaxial process. Micro-PL measurements on a single ZnO NMR containing luminescent QDs demonstrates that the light emission from QDs can be coupled to the nanorod cavity, resulting in shift of the micro-PL emission peak while keeping the micro-PL spectrum shape. The resulting structures will be attractive for a number of applications that aim at integrating ZnO devices such as laser cavities, waveguides, high-gain photodetectors and sensors, exspecially colourful light emission devices. Our paper demonstrates the first step towards the growth of ordered array of ZnO NMRs encapsulating QDs. Growth of highly ordered ZnO NMRs on substrates patterned by a photolithography process for device applications is underway and will be published elsewhere.

Publications

1. Liu, J., M. Notarianni, L. Rintoul, and N. Motta, *Encapsulation of nanoparticles into single-crystal ZnO nanorods and microrods.* **Beilstein Journal of Nanotechnology**, 2014. **5**: p. 485-493.
2. Liu, J. and N. Motta, *The nanonail flower.* **Materials Today**, 2014. **17**(6): p. 307-308.
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4. Mei Lyu, Jinzhang Liu, Jun Zhu*, Llew Rintoul, Nunzio Motta. *Encapsulating Quantum Dots into ZnO Nano and Micro Rods for Advanced Photonics Applications.* ***Advanced Device Materials (submitted)***

Conference presentations

1. Mei Lyu, Llew Rintoul, Jinzhang Liu, Nunzio Motta. Encapsulating Quantum Dots into ZnO Nano/Microrods for Advanced photonics Applications. Poster. **Nanostructures for Sensors, Electronics, Energy and Environment (NanoS-E3)** Kingscliff (NSW) Australia 27 September – 2 October 2015
2. 8th International Workshop on Zinc Oxide and Related Materials (IWZnO 2014), Sep 7-11, Niagara Falls, Ontario, Canada. (Poster presented by Jinzhang Liu).

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